

Lithium-Reactive Co₃(PO₄)₂ Nanoparticle Coating on High-Capacity LiNi_{0.8}Co_{0.16}Al_{0.04}O₂ Cathode Material for Lithium Rechargeable Batteries

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Metal ion dissolution from high-capacity $\text{LiN}_{0.8}\text{Co}_{0.16}\text{Al}_{0.04}\text{O}_2$ cathode material during storage at 90°C was completely blocked by a lithium-reactive $\text{Co}_3(\text{PO}_4)_2$ nanoparticle coating. As opposed to conventional coating methods, in which the coating material did not react with LiOH and Li₂CO₃ impurities dissolved from the cathode, the $\text{Co}_3(\text{PO}_4)_2$ coating material reacted with such impurities during annealing to form an olivine LiCoPO₄ phase on the bulk surface. Electrochemical properties of the optimized sample, annealed at 700°C for 5 h, demonstrated a 30% enhancement of the cycle life, compared to a bare sample without a loss in the first discharge capacity. Storage tests of the 4.3 V charged electrode at 90°C after 7 days showed that the bare sample was transformed into the spinel phase with a *Fd3m* space group, whereas the $\text{Co}_3(\text{PO}_4)_2$ -coated sample remained as a layered hexagonal phase with an $R\bar{3}m$ space group.

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Ni-based cathode materials have been intensively investigated for replacing currently used LiCoO₂ in Li-ion cells, $^{1-\dot{8}}$ but there are still several problems to be overcome. First of all, as opposed to LiCoO₂, Ni-based cathodes have rapid moisture uptakes, and both Li₂CO₃ and LiOH impurities were reported to be formed on the surface.⁹⁻¹¹ This resulted in gelation of the cathode slurry, accompanied by rapidly increased viscosity, resulting in irregular cathode coating thickness on Al foil. The second problem is related to structural instability above 60°C. It has been reported that Ni and active metal ions dissolve into the electrolytes upon storage at 90°C, with concurrent formation of Li₂CO₃ films on the particle surface.¹²⁻¹⁵ Both of these problems also led to severe gas evolution due to the decomposition of such impurity phases to H_2 or CO_x gases. A third problem is the substantial amount of oxygen evolved from the cathode above 200°C, which eventually leads to thermal runaway of the Li-ion cells.¹⁶⁻²¹ In general, oxygen evolution is accompanied by structural transformation, such as spinel and NiO-type rock salt structures.

In order to solve these technical hurdles, metal doping and coatings have been investigated. LiNi1/3Co1/3Mn1/3O2 has been reported to be the best composition to fulfill the requirements for Li-ion cells.^{22,23} However, due to its low electrode density and relatively low specific capacity (160 mAh/g), compared with high-Ni-content cathode materials with capacities higher than 180 mAh/g at 4.3 V, partial physical mixing with LiCoO₂ was suggested.¹⁵ TiO₂, Al₂O₃, SiO₂, and AlPO₄ coatings have been intensively investigated, and the cycle life and thermal stability of the materials were significantly improved, compared with bare samples. Among the coating candidates, the AlPO₄ coating, using water as a solvent, is the best choice in terms of $\cos t$,^{31,32} as well as electrochemical and thermal properties. However, dissolving Li impurities, such as LiOH and Li₂CO₃, from the cathodes was inevitable. These impurities did not react with the coating layer during annealing at 700°C and were expected to reprecipitate as LiOH and Li₂CO₃ on the particle surface. In accordance, these are termed as inactive coating materials with respect to lithium.

In this study, a lithium-reactive $Co_3(PO_4)_2$ coating was introduced for high-capacity $LiNi_{0.8}Co_{0.16}Al_{0.04}O_2$ cathode materials for Li-ion cells. This coating material reacted with Li impurities during annealing at 700°C. Electrochemical properties and structural changes upon storage at 90°C were characterized, using bare or coated cathodes.

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Experimental

In order to precipitate $Co_3(PO_4)_2$ nanoparticles, 0.38 g cobalt nitrate and 1 g (NH₄)₂HPO₂ were dissolved in 30 g distilled water. The nanoparticles, which were instantly pink in color and precipitated in the solution, were stirred for 20 min at pH \sim 5. To this solution, 100 g LiNi_{0.8}Co_{0.16}Al_{0.04}O₂ powder was added and mixed for 10 min, followed by drying and annealing at 120 and 700°C for 12 and 5 h, respectively, in air. LiNi_{0.8}Co_{0.16}Al_{0.04}O₂ powder with a particle size of 13 µm was prepared by mixing stoichiometric amounts of coprecipitated $Ni_{0.86}Co_{0.16}Al_{0.04}(OH)_2$ and $LiOH \cdot H_2O$ that were fired at 480 and 780°C for 4 and 15 h, respectively, at a molar ratio of 1:1.02. The detailed coprecipitation method of Ni_{0.80}Co_{0.16}Al_{0.04}(OH)₂ is described in Ref. 9. Figure 1 shows a schematic flow diagram for conventional AlPO₄ and $Co_3(PO_4)_2$ coating procedures for LiNi_{0.86}Co_{0.16}Al_{0.04}O₂. In the case of the AlPO₄ coating, in order to minimize the gelation and swelling from the decomposition of Li impurities on the particle surface at elevated temperatures, a washing procedure is required, whereas Co₃(PO₄)₂ does not need a washing process due to the reaction between the coating material and Li sources. Overall, the latter method is much more economical than the first one. The change in the pH of the powders (bare, AIPO₄-, and Co₃(PO₄)₂-coated samples after annealing at 700°C) immersed in water was monitored by adding 20 g powder to 50 mL purified water (pH \sim 7) with constant stirring with a magnetic stirrer. The pH was measured over a 40 min period. The powder was recovered by filtration when the pH had stabilized. In



Figure 1. (Color online) Schematic view of coating procedures for conventional AlPO₄ and novel $Co_3(PO_4)_2$ coatings.

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Figure 2. XRD patterns of precipitated $Co_3(PO_4)_2$ nanoparticles and asprepared LiCoPO₄, using firing of the mixture of 0.02 g LiOH·H₂O and 0.4 g $Co_3(PO_4)_2$ nanoparticles at 700°C for 7 h.

order to determine the moisture content (OH⁻) in the sample, a Karl–Fisher moisture titrator was used at 250°C (prior to measuring, the sample was vacuum-dried at 150°C for 2 h to remove the H₂O molecules adsorbed on the sample).

The cathodes for the battery test cells were made of cathode, super P carbon black, and polyvinylidene difluoride (PVDF) binder (Solef) in a weight ratio of 96:2:2. The slurry was prepared by thoroughly mixing an *N*-methyl-2-pyrrolidone (NMP) (Aldrich) solution of PVDF, carbon black, and the cathode material. The cointype half cells (2016R size), prepared in a helium-filled glove box, contained a cathode, a Li metal anode, a microporous polyethylene separator, and an electrolyte solution of 1 M LiPF₆ in ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 vol %).

High-resolution transmission electron microscopy (HRTEM) samples were prepared by the evaporation of the dispersed nanoparticles in acetone or hexane on carbon-coated copper grids. The fieldemission electron microscope was a JEOL 2000F operating at 200 kV. Powder X-ray diffraction (XRD) measurements were carried out using a Rigaku D/Max2000 with a Cu target tube. Inductively coupled plasma mass spectroscopy (ICP-MS; ICPS-1000IV, Shimadzu) was used to determine the metal content.

Results and Discussion

In order to confirm the possible formation of the LiCoPO₄ layer on the LiNi_{0.8}Co_{0.16}Al_{0.04}O₂ from the reaction between the precipitated Co₃(PO₄)₂ and the dissolved Li₂CO₃ and LiOH impurities from the active cathode material during the coating process, first the dissolved amounts of the impurities from the cathode during the coating process were estimated using a titration method.⁹ When the 100 g cathode powder was dissolved in the coating solution in 30 mL distilled water, 0.02 g Li sources were dissolved from the cathodes. Also, 0.4 g of Co₃(PO₄)₂ nanoparticles were precipitated when 0.38 g cobalt nitrate and 1 g (NH₄)₂H₂PO₄ were used. Second, we assumed that 0.02 g of LiOH·H₂O and 0.4 g of Co₃(PO₄)₂ nanoparticles reacted completely with each other at 700°C for 5 h, forming lithium-deficient Li_xCoPO₄. These assumptions are supported by the following results.

Figure 2 exhibits the XRD patterns of precipitated $Co_3(PO_4)_2$ and LiCoPO₄ obtained from the above scheme. The obtained LiCoPO₄ can be identified as a pure olivine structure.³³ From this result, we can expect that the Li_xCoPO₄ layer may be formed on the particle surface after annealing by the reaction with $Co_3(PO_4)_2$ and



Figure 3. TEM images of (a) bare and (b) Co₃(PO₄)₂-coated samples.

Li impurities. However, we cannot eliminate the possibility of additional Li contribution from the bulk during the formation of LiCoPO₄, as well as possible formation of the solid solution phase between LiCoPO₄ and the bulk. Figure 3 shows TEM images of the bare and $Co_3(PO_4)_2$ -coated sample surfaces, and the bare sample did not show any coating layer, as usually observed in coated samples.²⁴⁻³² Coating concentration of the sample after annealing at 700°C was estimated to be ~ 1 wt % by using ICP-MS analysis of the P element. The *d*-spacing value of the bare sample corresponds to the (104) lattice fringe of the layered hexagonal phase. The coated sample showed 3.45 and 2.49 Å d-spacing values at the particle surface, corresponding to (111) and (311) lattice fringes of the olivine LiCoPO₄ phase, respectively,³⁴ confirming the above assumption. Previously our result showed that the 1 wt % AlPO₄ coating concentration approximately corresponded to $\sim 20 \text{ nm}$ coating thickness.³¹ However, the AlPO₄ coating layer did not react with the bulk phase during annealing, thus forming a distinguishable coating layer to the bulk phase. However, in the case of $Co_3(PO_4)_2$ coating, the coating layer reacted with Li impurities such as LiOH and LI₂CO₃ and Li in the bulk, resulting in the formation of Li_rCoPO₄. Accordingly, the Li_xPO₄ coating layer is not easy to distinguish from the bulk phase, as supported by Fig. 3.

Figure 4 shows XRD patterns of the bare and coated cathode powders and phase can be indexed with hexagonal-type layered structure with an $R\overline{3}m$ space group without showing secondary



Figure 4. XRD patterns of the bare and coated cathode powders.

phases. Lattice constants *a* and *c* of the bare and coated sample are quite similar to each other, showing a = 2.8631(4), c = 14.165(7) and a = 2.8621(6), c = 14.164(3), respectively.

Figure 5 exhibits the voltage profiles of the bare and the coated samples annealed at 700°C for 5 h at 0.1, 0.2, 0.5, and 1 C rates and after 40 cycles at a rate of 1 C between 3 and 4.3 V (1 C rate was set at 190 mA/g). After coating, the first discharge capacity and irreversible capacity ratio of 190 mAh/g and 10%, respectively, were similar to the bare sample. (The discharge curves were obtained from using the same sample.) However, the discharge capacity of the first 1 C cycling was 173 mAh/g, which is higher than the bare sample (160 mAh/g), and the capacity retention of the coated samples after 40 cycles was 149 mAh/g, which is 30% higher than the bare sample. Olivine-type material is known to have low electronic conductivity, but this is the case for the bulk material. In our case, the electrical conductivity of the nanometer-scale olivine coating layer is believed to be much improved, compared with the bulk analogue, because the C-rate performance of the coated sample was not affected by the coating layer, as shown in Fig. 5b. Such improvement is believed to be that the nanometer-scale olivine layer helps the electrical conduction due to the reduced surface scattering that enhanced the total resistivity of the material.

Figure 6 shows the pH changes in the bare and $Co_3(PO_4)_2$ -coated samples, compared with a AlPO₄-coated sample, as a function of time. As soon as the bare and AlPO₄-coated powders had been



Figure 5. Voltage profiles of the bare and the coated samples, annealed at 700°C for 5 h at 0.1, 0.2, 0.5, and 1 C rates, and after 40 cycles at a rate of 1 C between 3 and 4.3 V (1 C rate set at 190 mA/g).



Figure 6. pH changes in the bare and $Co_3(PO_4)_2$ -coated samples as a function of time, compared with an AlPO₄-coated sample.

placed into the water, the pH rapidly increased to 12.5 and stabilized at this value. This indicates that Li impurities on the cathodes (Li₂CO₃ and LiOH) were dissolved into the solution, and lithium impurities were not removed even after AlPO₄ coating. However, the Co₃(PO₄)₂-coated sample showed the lowest value of pH at 10.5, indicative of complete reaction of lithium impurities with the coating material during annealing. This is comparable to washed LiCoO₂ that showed a pH value of 10.5 at the same conditions.⁹ This result implies that washing is inevitable for conventional AlPO₄ coatings.

A slow and spontaneous reduction of Ni³⁺ to Ni²⁺ happens for the cathode material during storage. Correspondingly, lattice oxygen O⁻ is oxidized to active oxygen O²⁻, followed by the weakening of the Ni–O bond. Then, a disproportionating reaction of active oxygen O²⁻ produced on the surface combines with CO₂ and H₂O in air to form Li₂CO₃ and LiOH on the surface of the cathode.¹⁰ This oxygen undergoes reactions with CO₂/H₂O in air, according to the following reaction

$O^{2-} + CO_2/H_2O \rightarrow CO_3^{2-}/2OH^{-}$

which is believed to react with LiPF_6 , producing acidic HF in the electrolytes. HF can then easily dissolve the Ni⁴⁺ and Co³⁺ metal ions. This result indicates that the olivine LiCoPO₄ phase is very effective in minimizing metal dissolution.

Figure 7 exhibits XRD patterns of the bare electrode before and after charging at 4.3 V under various conditions. When the layered phase is transformed to the spinel phase, two sets of (006)/(012)and (018)/(110) peaks merge into the single ones. In addition, a peak at ~18.5° (marked as $\mathbf{\nabla}$ in Fig. 7) shifts to higher angles. Because the (110) peak is superimposed with an Al peak at 65° (dotted lines in Fig. 6 and 7), the merging (018) and (110) peaks into the single peak is not readily observed in the bare and coated samples, especially the samples stored at 90°C. However, the change of the peak distance between the (018) and (110) peaks in the XRD pattern of the 4.3 V charged sample and subsequently stored samples at 90°C can provide useful information on the possible phase transition. In the XRD pattern the charged bare samples stored at 90°C did not show any noticeable changes for 1 day, implying that the original layered structure with an $R\overline{3}m$ space group was sustained. After 7 days storage at 90°C, the peaks shifted to higher angles and both (018)/(110) and (006)/(102) peaks merged into the single peaks, indicating the formation of the spinel LiNi2O4 phase (Fd3m) (JCPDS no. 41-0890).

Table I shows that dissolution amounts of Ni and Co ions into the electrolytes during storage, using both the bare and the coated samples, were monitored for the following conditions: 1 and 7 days at room temperature and 90°C, as well as 1 and 7 days at 90°C after 4.3 V charging. After charging the cells, the electrodes were separated from the cell and kept in electrolytes (10 mL) for designated



Figure 7. XRD patterns of the bare electrode before charging and after charging at 4.3 V at various storage conditions.

times. Both bare and coated samples did not show any noticeable metal dissolution, even after storage at 90°C for 1 day (4.3 V charging). However, the amounts of Co and Ni ions dissolved increased to 90 and 250 ppm, respectively, after 7 days of storage at 90°C (after 4.3 V charging). The coated samples stored at 90°C for 1 day of storage (after 4.3 V charging) resulted in negligible amounts of Ni and Co ions dissolved, which were 1.2 and 2.4 ppm, respectively, after 7 days at 90°C. We believe that such Ni⁴⁺ ion dissolution initiates structural rearrangement from the layered to the spinel phase. We further carried out TEM analysis of the charged bare sample after storage at 90°C for 7 days, as shown in Fig. 8. Figure 8a shows the surface morphology of the stored sample and many surface roughnesses can be observed. This is indicative of surface defects generated by the Ni⁴⁺ ion dissolution. Figure 8b exhibits the HRTEM image of Fig. 8a, and a lattice fringe of the (311) plane corresponding to 2.42 Å of spinel LiNi₂O₄ phase.

Table I. ICP-MS results of Ni and Co in the charged bare and coated charged samples stored at 90°C for 1 and 7 days.

	Ni (ppm)	Co (ppm)
Bare sample before storage	2	1.8
Bare sample after 1 day	9.7	3.4
Bare sample after 7 days	250	90
Coated sample before storage	0.9	1.4
Coated sample after 1 day	1.2	2.2
Coated sample after 7 days	1.4	2.4

After storage at 90°C for 7 days, all the diffraction peaks are assigned to a spinel phase with a lattice constant of 8.083 Å. In general, the transformation of the layered structure with an $R\bar{3}m$ space group to the spinel phase (Fd3m) requires a migration of 25% of the transition metal ions from 3b octahedral sites (metal layer) into 3a octahedral sites (lithium layer). Our Rietveld refinement result showed 10% of the (Ni,Co)^{3+/4+} ions in the 16C sites, indicating that the migration of the transition metal ions from the nickel layer into the lithium layer to produce a spinel structure is incomplete at 90°C. This is the first evidence for the phase transformation to a spinel phase at the very low temperature of 90°C, as compared with previous studies that showed the spinel transition above 150°C.^{1,18} The calculation of the cation migration of the bare sample after storage is based on spinel structure because its XRD pattern supported the phase transformation into the spinel.

The XRD patterns of the coated samples stored at 90°C for 1 and 7 days are different from those of the bare samples at the same storage condition and do not show the peaks merging in two sets of (018)/(110) and (006)/(102) peaks (Fig. 9). Generally, (006) and (102) peaks get to merge with delithiation in the cathode material, but the coated sample still shows the peaks splitting. At this time, we do not know the origin of such phenomena, but we suspect that coating may affect the microstructure of the cathode material. In addition, peaks shifted to higher angles are not observed. These results mean that the coated sample did not show the phase transition to a spinel phase even after 7 days of storage at 90°C after 4.3 V charging. Because the XRD pattern of the coated cathodes after 7 days storage at 4.3 V could be indexed with a hexagonal-type layered structure with an $R\overline{3}m$ space, we did not consider the possible cation migration that led to structural transformation into the spinel phase. The structural transformation starts on the particle surface by the metal dissolution and chemically stable LiCoPO₄ phase is effective to reduce the metal dissolution. The TEM images of the stored cathode in Fig. 10 show smooth surfaces, as opposed to those of the bare cathode (Fig. 8), and a lattice fringe of the (311) plane of the LiCoPO₄ phase corresponding to 2.50 Å is observed.



Figure 8. TEM images of bare electrode after charging at 4.3 V and subsequent storage at 90° C for 7 days.



Figure 9. XRD patterns of the coated electrode before charging and after charging at 4.3 V at various conditions.

Conclusion

A lithium-reactive $\text{Co}_3(\text{PO}_4)_2$ nanoparticle coating $\text{LiNi}_{0.8}\text{Co}_{0.16}\text{A}_{10.04}\text{O}_2$ resulted in the formation of a Li_xCoPO_4 coating layer after annealing at 700°C. As opposed to conventional coating methods that could not remove the LiOH and Li_2CO_3 impurities, the $\text{Co}_3(\text{PO}_4)_2$ coating reacted with such impurities during the annealing process, thus minimizing any side reactions with electrolytes. Upon prolonged storage of the charged cathode (4.3 V) at 90°C, the coated cathode sustained the original layered phase while the bare cathode was transformed into the spinel phase, possibly due to the dissolution of Ni⁴⁺ ions into the electrolytes.

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References

- I. Belharouak, W. Lu, D. Vissers, and K. Amine, *Electrochem. Commun.*, 8, 329 (2006).
- J. Cho, T.-J. Kim, J. Kim. M. Noh, and B. Park, J. Electrochem. Soc., 151, A1899 (2004).
- H. Omanda, T. Brousse, C. Marhic, and D. M. Schleich, J. Electrochem. Soc., 151, A922 (2004).
- 4. Y. Lee, M. G. Kim, J. Kim, Y. Kim, and J. Cho, *J. Electrochem. Soc.*, **152**, A1824 (2005).
- H. Arai, M. Tsuda, K. Saito, M. Hayashi, and Y. Sakurai, *Solid State Ionics*, 109, 295 (1998).
- M. Yoshio, H. Noguchi, J.-I. Itoh, M. Okada, and T. Mouri, J. Power Sources, 90, 176 (2000).
 I. Choi and A. Manthiram Electrochem Solid-State Lett. 8 C102 (2005).
- J. Choi and A. Manthiram, *Electrochem. Solid-State Lett.*, 8, C102 (2005).
 K. M. Shaju, G. V. Subba Rao, and B. V. R. Chowdari, *J. Electrochem. Soc.*, 151,
- A1324 (2004).J. Kim, Y. Hong, K. S. Ryu, M. G. Kim, and J. Cho, *Electrochem. Solid-State Lett.*,
- 9, A19 (2006).
 10. H. S. Liu, Z. R. Zhang, Z. L. Gong, and Y. Yang, *Electrochem. Solid-State Lett.*, 7,
- A190 (2004).
 K. Matsumoto, R. Kuzuo, K. Takeya, and A. Yamanaka, J. Power Sources, 81-82, 558 (1999).
- D. Aurbach, K. Gamolsky, B. Markosky, G. Salitra, Y. Gofer, U. Heider, R. Oesten, and M. Schmidt, *J. Electrochem. Soc.*, 147, 1322 (2000).
- S. W. Song, G. V. Zhuang, and P. N. Ross Jr., J. Electrochem. Soc., 151, A1162 (2004).
- A. M. Andersson, D. P. Abraham, R. Haasch, S. MacLaren, J. Liu, and K. Amine, J. Electrochem. Soc., 149, A1358 (2002).
- 15. M. Noh, Y. Lee, and J. Cho, J. Electrochem. Soc., 153, A935 (2006).
- 16. J. Cho, H. Kim, and B. Park, J. Electrochem. Soc., 151, A1707 (2004)
- Y. Lee, M. G. Kim, J. Kim, Y. Kim, and J. Cho, J. Electrochem. Soc., 152, A1824 (2005).
- M. Guilmard, L. Croguennec, D. Denux, and C. Delmas, *Chem. Mater.*, **15**, 4476 (2003).
- K. K. Lee, W. S. Yoon, K.-B. Kim, K. Y. Lee, and S.-T. Hong, J. Power Sources, 97-98, 321 (2001).
- 20. K. K. Lee, W. S. Yoon, and K. B. Kim, J. Electrochem. Soc., 148, A1164 (2001).
- 21. J. Cho, Chem. Mater., 13, 4537 (2001).
- 22. N. Yabuuchi and T. Ohzuku, J. Power Sources, 119, 171 (2003).
- M. G. Kim, H. J. Shin, J.-H. Kim, S.-H. Park, and Y.-K. Sun, J. Electrochem. Soc., 152, A1320 (2005).
- 24. J. Cho, Y. J. Kim, T.-J. Kim, and B. Park, Angew. Chem., Int. Ed., 40, 3367 (2001).
- J. Cho, Y. J. Kim, and B. Park, *Chem. Mater.*, **12**, 3788 (2000).
 J. Cho, J.-G. Lee, B. Kim, and B. Park, *Chem. Mater.*, **15**, 3190 (2003).
- 27. J. Cho, Y. J. Kim, and B. Park, J. Electrochem. Soc., 148, A1110 (2001)
- 28. Z. R. Zhang, H. S. Liu, Z. L. Gong, and Y. Yang, J. Electrochem. Soc., 151, A599 (2004).
- Y. J. Kim, H. Kim, B. Kim, D. Ahn, J.-G. Lee, T.-J. Kim, D. Son, J. Cho, Y.-W. Kim, and B. Park, *Chem. Mater.*, **15**, 1505 (2003).
- 30. J. Cho, Electrochem. Commun., 5, 146 (2003).
- J. Cho, Y.-W. Kim, B. Kim, J.-G. Lee, and B. Park, Angew. Chem., Int. Ed., 42, 1618 (2003).
- 32. J. Cho, J.-G. Lee, B. Kim, and B. Park, Chem. Mater., 15, 3190 (2003).
- K. Amine, H. Yasuda, and M. Yamachi, *Electrochem. Solid-State Lett.*, 3, 178 (2000).
- JCPDS Card No. 85-0002, International Center for Diffraction Data, Newtown Square, PA (2001).
- Nanostructures and Nanomaterials, G. Cao, Editor, World Science Publishing, Singapore (2004).



Figure 10. TEM images of the coated electrode after charging at 4.3 V and subsequent storage at 90°C for 7 days.